

CLAIMS

1. Segment copolymers comprising segments "A" having polyvinylpyrrolidone (PVP) structure and segments "B" having a polyester structure.
2. Segment copolymers as claimed in claim 1 in the form of linear A-B type
5 copolymers.
3. Segment copolymers as claimed in claim 2 wherein the structure is of the type

$$\text{PVP-COO-(R}^3\text{-COO)}_n\text{H,}$$
or of the type:

$$\text{PVP-(OOC-R}^3\text{)}_n\text{OH,}$$

10 where n is a number between 5 and 500, and R is a linear or branched hydrocarbon chain containing from 1 to 12 carbon atoms.
4. Segment copolymers as claimed in claim 3 wherein n is comprised between 15 and 150, R³ has from 1 to 6 carbon atoms.
5. Segment copolymers as claimed in claim 1 in the form of linear copolymers of
15 A-B-A type.
6. Copolymers as claimed in claim 5 wherein the structure is of the type

$$\text{PVP-COO-(R}^1\text{-OOCR}^2\text{COO)}_n\text{-R}^1\text{-OOC-PVP,}$$
or of the type:

$$\text{PVP-(OOC-R}^1\text{-COOR}^2\text{)}_n\text{OOCR}^1\text{COO-PVP}$$

20 where n is a number between 5 and 300, and R¹ and R² can be equal or different, and are linear or branched hydrocarbon chains having from 1 to 25 carbon atoms.
7. Segment copolymers as claimed in claim 6 wherein n is comprised between 10 and 100 and R¹ and R² have from 1 to 8 carbon atoms.
8. Segment copolymers as claimed in claim 1 being branched or hyperbranched ,
25 wherein the PVP segments are located at the terminal ends of the branches.
9. Segment copolymers as claimed in claim 8, having the formula represented in Figure 1, wherein A is polyvinylpyrrolidone, D is the residue deriving from a polycarboxylic or polyol, wherein the hydroxy or carboxy functions are at least 3, (BC) indicate the repeating unit of the B polyester segment and n is comprised
30 between 2 and 200.
10. Copolymers as claimed in claim 1 being in the form of branched or hyperbranched copolymers having located at the ends of the branches;

- PVP segments and residues derived from monocarboxylic acids R-COOH, or monohydroxylated alcohols of the R-OH type where R is a linear or branched hydrocarbon chain containing from 1 to 25 carbon atoms,
 - PVP segments or residues derived from dicarboxylic acids HOOC-R-COOH or dihydroxylic alcohols of the HO-R-OH type where R is a linear or branched hydrocarbon chain as aforedefined.
11. Segment copolymers as claimed in claim 10, wherein R has from 1 to 8 atoms.
12. Segment copolymers as claimed in anyone of claims 10 and 11 as represented in Figure 2, wherein the A indicates the polyvinylpyrrolidone chains D is the residue deriving from a polycarboxylic or polyol, wherein the hydroxy or carboxy functions are at least 3, (BC) indicate the repeating unit of the B polyester segment n is comprised between 2 and 200, and E is the residue of a monofunctional alcohol.
13. Segment copolymers as claimed in anyone of claims 8 to 13, wherein the branching sites consist of polyol or polycarboxylic acid residues having a number of functions (hydroxyl or carboxyl respectively) between 3 and 12.
14. Segment copolymers as claimed in claim 13 wherein said number of function of the polyol or polycarboxylic acid is comprised between 3 and 6.
15. Segment copolymers as claimed in any one of claims 8-14, wherein the molar ratio between the number of branching sites and polyester fragments is comprised between 0.01 and 2,
16. Segment copolymers as claimed in claim 15, wherein said ratio is comprised between 0.1 and 1.5.
17. Segment copolymers as claimed in anyone of claims 8-15, wherein the molar ratio between the number of branching sites and PVP fragments is comprised between 0.01 and 100,
18. Segment copolymers as claimed in claim 17 wherein said molar ratio is comprised between 0.1 and 10.
19. Segment copolymers as claimed in any one of claims 8-18 in cross-linked form.
20. Segment copolymers as claimed in claim 1 wherein the PVP segments are

comb-grafted at one end onto polyester chains.

21. Segment copolymers as claimed in anyone of claims 1-20 wherein the PVP segments have a weight average molecular weight between 600 and 15,000.

22. Segment copolymers as claimed in claim 21 wherein said A (PVP) segment
5 has a weight average molecular weight comprised between 1,000 and 6,000.

23 Segment copolymers as claimed in anyone of claims 1-22, having a PVP content by weight between 5% and 95%.

24. Segment copolymers as claimed in claim 23 wherein said PVP content is comprised between 10% and 50%.

10 25. Segment copolymers as claimed in anyone of claims 1-24, having a weight average molecular comprised between 10,000 and 1,000,000.

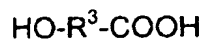
26. Segment copolymers as claimed in claim 25, wherein said average molecular weight is comprised between 20,000 and 200,000.

27. A process for preparing the copolymer as claimed in claim 2, comprising
15 carrying out a polycondensation reaction on PVP terminated at one end with a hydroxy or carboxy function with respectively :

- a biacid or a bialcohol in the presence of a monoalcohol or a monocarboxylic acid or in alternative
- a hydroxy carboxylic acid optionally a cyclic derivative thereof,

20 with the proviso that ratio of total moles of OH function /total moles of COOH functions is =1.

28. The process according to claim 27 for preparing the copolymers of claim 3, comprising effecting polycondensation between PVPs monofunctionalized at one end with hydroxyl or carboxyl groups optionally in the form of methyl or ethyl
25 esters, in the presence of hydroxycarboxylic acids of type

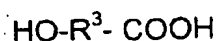


where R^3 is a linear or branched hydrocarbon chain with between 1 and 12 carbon atoms.

29. The process according to claim 28, wherein R^3 has from 1 to 6 carbon atoms.

30 30. The process according to claim 27 for preparing the copolymers of claims 3, comprising effecting ring-opening polycondensation on PVP monofunctionalised at one end with hydroxyl or carboxyl groups optionally in the form of methyl or

ethyl esters with cyclic derivatives selected from lactones, glycolides or lactides of the hydroxy acids of formula



where R^3 is a linear or branched hydrocarbon chain with between 1 and 12 carbon atoms.

31. The process as claimed in claim 30, where R^3 has from 1 to 6 carbon atoms.

32. A process for preparing the copolymers as claimed in claim 5 comprising carrying out a polycondensation reaction on PVP terminated at one end with a hydroxy or carboxy function with a biacid or a bialcohol with the proviso that the ratio of total moles of OH function/total moles of COOH functions is ≈ 1 .

33. The process as claimed in claim 32 for preparing the copolymers of claims 6 and 7, comprising effecting polycondensation reaction between PVPs monofunctionalized at one end with hydroxyl or carboxyl groups optionally in the form of methyl or ethyl esters, and mixtures of dicarboxylic acids and diols of respectively general formula $\text{HOOC-R}^1\text{-COOH}$ and $\text{HO-R}^2\text{-OH}$ where R^1 and R^2 , equal or different, are linear or branched hydrocarbon chains containing from 1 to 25 carbon atoms.

34. The process according to claim 33 wherein R^1 and R^2 have from 1 to 8 carbon atoms.

35. A process for preparing the copolymers of claims 8 and 9, comprising effecting polycondensation of the mixtures in variable proportions of:

a) PVPs monofunctionalized at one end with hydroxyl or carboxyl groups optionally in the form of methyl or ethyl esters;

b) dicarboxylic acids and diols;

c) polyols or polycarboxylic acids having at least 3 hydroxyl or carboxyl functions, provided that:

i), when said copolymers are not crosslinked

r is $< r_c$

ii) when said copolymers are crosslinked

r is $> r_c$

$r = N_{a0}/N_{b0}$, N_{a0} indicates the initial total number of hydroxy or carboxy function

in defect, Nb_0 indicates the total initial number of carboxy or hydroxy functions in excess,

$$r_c = \frac{1}{(f_{w,A}-1)(f_{w,B}-1)}$$

5 where $f_{w,A}$ and $f_{w,B}$ are the "weight" averages of the functionalities of the monomers present, including monoalcohol or monocarboxylic acid.

36. The process according to claim 35, wherein the diols and the diacids are of respectively general formula $\text{HOOC-R}^1\text{-COOH}$ and $\text{HO-R}^2\text{-OH}$, where R^1 and R^2 , equal or different, are linear or branched hydrocarbon chains containing from 1 to
10 25 carbon atoms.

37. The process according to claim 36 wherein R^1 and R^2 have from 1 to 8 carbon atoms.

38. The process according to anyone of claims 35-37, wherein the polyols or polycarboxylic acids have respectively per molecule between 3 and 12 hydroxy or
15 carboxy functions.

39. The process according to claim 38, wherein the polyols or polycarboxylic acids have respectively per molecule between 3 and 6 hydroxy or carboxy functions.

40. A process for preparing the copolymers as claimed in anyone of claims 10-12, comprising effecting a polycondensation of mixtures in various proportions of:

- 20 a) PVPs monofunctionalized at one end with hydroxyl or carboxyl groups optionally in the form of methyl or ethyl esters;
b) dicarboxylic acids and diols;
c) polyols or polycarboxylic acids having least 3 hydroxyl or carboxy functions
d) monocarboxylic acids of type R-COOH or monohydroxylated alcohols of type
25 ROH , where R has the aforementioned meanings provided that:

i), when said copolymers are not crosslinked

" r " is $< r_c$

ii) when said copolymers are crosslinked

30 " r " is $> r_c$

$r = Na_0/Nb_0$, Na_0 indicates the initial total number of hydroxy or carboxy function in defect, Nb_0 indicates the total initial number of carboxy or hydroxy functions in excess,

$$r_c = \frac{1}{(f_{w,A}-1)(f_{w,B}-1)}$$

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where $f_{w,A}$ and $f_{w,B}$ are the "weight" averages of the functionalities of the monomers present, including monoalcohol or monocarboxylic acid.

41. The process according to claim 40 wherein the diols and the diacids are of respectively general formula $\text{HOOC-R}^1\text{-COOH}$ and $\text{HO-R}^2\text{-OH}$, where R^1 and R^2 ,
10 equal or different, are linear or branched hydrocarbon chains containing from 1 to 25 carbon atoms.

42. The process according to claim 41, wherein R^1 and R^2 have from 1 to 8 carbon atoms.

43. The process according to anyone of claims 41 and 42, wherein the polyols or
15 polycarboxylic acids have respectively per molecule between 3 and 12 hydroxy or carboxy functions.

44. The process as claimed in claim 43, wherein the polyols or polycarboxylic acids have respectively per molecule between 3 and 6 hydroxy or carboxy functions.

20 45. Process for preparing the copolymers of claim 20, comprising effecting ring-opening polymerisation of mixtures of PVP terminating at one end with a lactone, alone or optionally with the same or a different lactone from the previous one.

46. The process as claimed in claim 45, carried out on PVP terminating with γ -butyrolactone, in the presence of γ -butyrolactone.

25 47. A process for preparing the copolymers according to claim 20 comprising effecting a chain transfer polymerization reaction with N-vinyl pyrrolidone in the presence of PLGA as the chain transfer agent.

48. The process according to claim 47, further comprising a second chain transfer polymerization, wherein the chain transfer agent is methyl isobutyrate.

30 49. A composition comprising the segment copolymers according to anyone of

claims 1-20, and an ingredient having therapeutic or cosmetic activity, or a dietary supplement.

50. Use of copolymers claimed in claims 1-26 for preparing blends with copolymers of poly(lactic-glycolic) acid (PLGA) of various molecular weight.